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PRODUCTION TECHNOLOGY FOR GYPSUM-CERAMIC MATERIAL

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A technology for producing a gypsum-ceramic material based on acid fluoride is developed. Its composition and properties are determined using physicochemical analysis methods. The material developed can be ground and polished and has a surface texture resembling marble.

In the production of ceramic materials based on acid fluoride, for the purpose of increasing strength and water resistance of acid fluoride composites [1] the behavior of acid fluoride was investigated in a high temperature range using such flux as technological sewage from oil field, which is a 32%-solution of mineral salts with prevalence of sodium chloride.

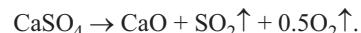
It was noted [2] that acid fluoride can be used in the production of gypsum-ceramic materials with increased strength and water resistance. The material obtained in this way is less expensive, has good decorative properties, and does not accumulate static electricity.

In batch preparation (RF Patent No. 2201904) acid fluoride is crushed in a roller mill ensuring crushing of particles to 2 mm. Next, a mineralizing additive to the batch is prepared including sodium phosphate and sodium silicate solution in an amount of 15% of dry acid fluoride weight. The optimum ratio between the additive components is 1 : 2, respectively. The moisture of the mixture containing acid fluoride, sodium silicate solution, and sodium phosphate before molding was at a level of 10–15%.

Articles were compressed in a mold at specific pressure of 15 MPa. The heating rate in firing samples was 200 K/h, the duration of isothermal exposure at 850°C was 30 min, and cooling proceeded at a rate of 200 K/h. After firing the articles were polished to reveal their texture, which is comparable to marble in its exterior appearance.

Firing of products is accompanied by release of gaseous compounds that need to be utilized to improve environmental safety of gypsum-ceramic production. In this context, qualitative and quantitative analysis of released gases was performed using gas-adsorption chromatography (Fig. 1). The analysis demonstrated that at a temperature of 400–420°C residual sulfuric acid, which forms part of the acid fluoride, decomposes into SO_2 , O_2 , and H_2O , which in a gaseous state are emitted in the atmosphere. As the tempera-

ture increased to over 660°C, acid fluoride partly decomposes according to the following scheme:



Since the maximum admissible concentration of SO_2 in air is 10 mg/m³, SO_2 needs to be utilized by recovering the released gas into the technological cycle. A laboratory set was designed to model the processes occurring in firing articles (Fig. 2).

A sample of acid fluoride 2 previously weighed on an analytical scale was placed in a combustion boat in a firing furnace 1. The firing temperature was monitored using thermocouple 3 and voltmeter 4. The experiment was carried out at

Fig. 1. Chromatogram of gases CO_2 (a) and SO_2 (b) released from acid fluoride: a) after 4.5 min at a temperature of 63°C; b) after 16 min at a temperature of 110°C.

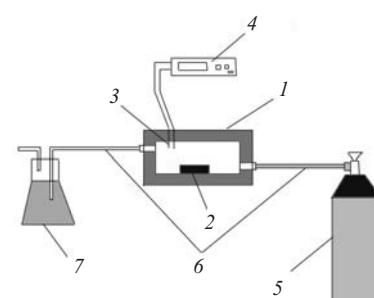
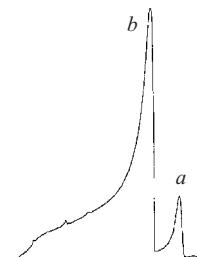


Fig. 2. Laboratory set for sampling and determination of the quantity of gas emitted.

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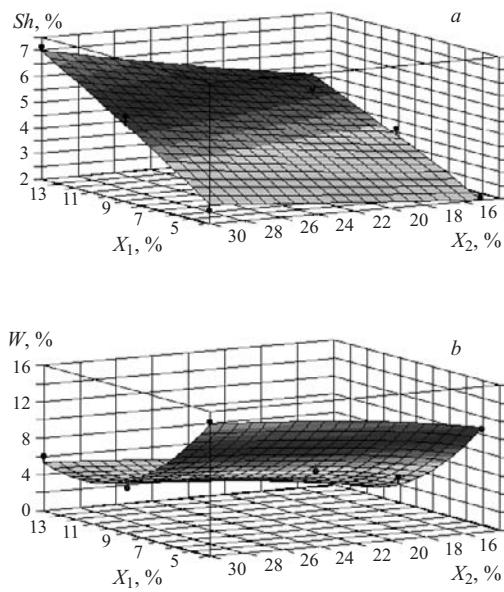


Fig. 3. Variation in fire shrinkage Sh (a) and water absorption W (b): X_1 and X_2 are the mass contents of sodium phosphate and sodium silicate solution, respectively.

750°C for 1.5 h. In the course of firing, nitrogen was fed from a cylinder 5 via an airtight system 6 so that the sulfur oxide emitted in the firing of acid fluoride enters into a flask 7 with a recovering liquid.

The liquid was a solution of caustic soda previously nitrated by a hydrochloric acid solution in the presence of methyl orange until the color of the indicator changed from yellow-orange to pink, which corresponds to a weakly acid medium. In repeated titration after firing it was found that 20.2 mg of SO_3 had been emitted per 1 g of acid fluoride, which corresponds to decomposition of 3.4% $CaSO_4$. As a result, the following chemical reactions take place:



All compounds (Na_2SO_4 , Na_2SO_3 , $NaHSO_3$, $NaHCO_3$) are formed at the stage of mixing and during molding.

Thus, modeling the batch firing process made it possible to identify the composition and volume of gases released and to control the process of saturation of the solution with gases and their recovery in the technological cycle.

The studies indicated that as the quantity of sodium silicate solution grows from 15 to 30%, with a 5% content of sodium phosphate, fire shrinkage increases from 2.1 to 2.6%, and with a 15% content of sodium silicate solution and sodium phosphate increased from 5 to 10%, fire shrinkage grows from 2.1 to 3.5%. This tendency persists in a further increase in the content of these additives.

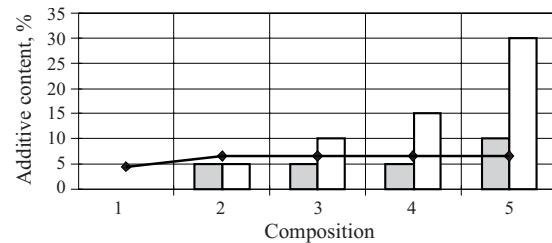


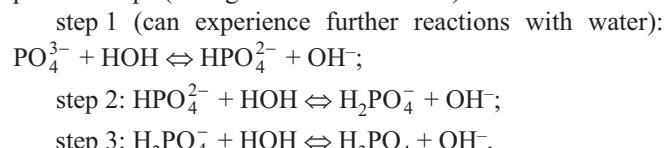
Fig. 4. Experimental pH values of gypsum-ceramic compositions modified by sodium silicate solution and sodium phosphate: (■) content of sodium phosphate; (□) content of sodium silicate solution; (—◆—) pH of aqueous extract.

Figure 3a shows the variations in fire shrinkage of gypsum ceramics depending on the content of sodium silicate solution and sodium phosphate. The dependence of fire shrinkage on additive content is described by a linear function. With increasing content of sodium silicate solution, as well as sodium phosphate, fire shrinkage grows.

The water absorption of all samples of the optimum composition was measured as well. After the experiments, a mathematical model was constructed, and the confidence interval with degree of probability was determined for each experimental value.

The water absorption variation depending on the content of sodium phosphate additive is described by a parabolic function (Fig. 3b). With increasing content of sodium silicate solution additive, the type of function does not change but is shifted toward higher water absorption.

The pH values of aqueous extracts were measured for all samples. In samples sintered from acid fluoride and exposed in water, pH = 4.5. This is due to the presence of residual sulfuric acid former in the production of hydrofluoric acid from fluorite in industrial conditions. When the composition consisting of acid fluoride and sodium phosphate is exposed in water, electrolytic dissociation of the high-base salt takes place in steps (strong base and weak acid):



However, the second and third stages of hydrolysis are expressed less perceptibly. This is due to the fact that the product of the first step of hydrolysis dissociates significantly better than the products of steps 2 and 3. At the same time, the pH of the medium at the early stage of reaction with water grows significantly up to 11. After exposure in water for 7 days, the pH decreases to 5 in samples obtained from acid fluoride and sodium phosphate. This is due to the fact that acid compounds $Na_2HPO_4 \cdot 12H_2O$, NaH_2PO_4 , $Ca(H_2PO_4)_2$ and $NaHSO_4$ formed in reactions with water have dissolved in water and do not influence pH any longer.

The reaction proceeds until chemical equilibrium is reached, i.e., until the formation of compounds difficultly

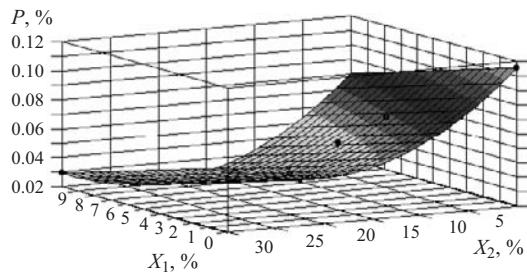


Fig. 5. Variation in porosity P depending on mass content of sodium phosphate X_1 and sodium silicate solution X_2 .

soluble in water such as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and insoluble in water such as $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.

The pH index of samples modified by sodium phosphate and sodium silicate solution is equal to 6.5 and has a neutral medium. The pH level in this case does not depend on the content of sodium phosphate and sodium silicate solutions (Fig. 4).

Changes in specific porosity of gypsum ceramics take place due to different contents of additives (Fig. 5). Upon adding various quantities of sodium phosphate (initial content 5%) to the initial acid-fluoride mixture, the porosity decreases. On further increase in the additive content, the structure of material becomes visibly laminar. It becomes brittle. The porosity of the modified material increases compared to initial material, which produces a decrease in strength.

The decrease in porosity of gypsum ceramics not exposed in water with increasing contents of sodium phosphate and sodium silicate solution is related to the production of the melt under thermal treatment, a decrease in specific surface area and, consequently, a decrease in interparticle voids. After the samples are held in water, the pores, in addition to emerging melts, become filled with crystal hydrates of gyp-

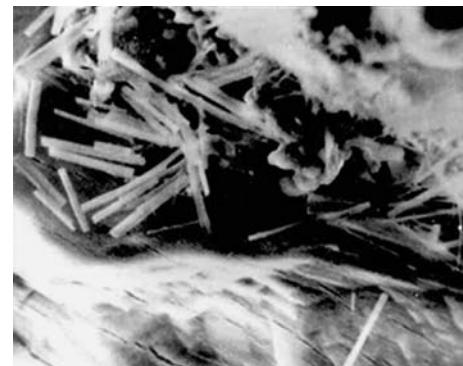


Fig. 6. Pores filled with gypsum and brushite hydrocristals ($\times 2100$).

sum, brushite, and hydrosilicates, which more intensely decreases the porosity of materials (Fig. 6).

Thus, to obtain a gypsum-ceramic material, one should use traditional technology of ceramic production. At the same time, one should take into account gas emission in the firing of gypsum ceramic materials. To neutralize these gases, an additional process stage is needed, including recovery of emitted gases in the technological cycle, which will make it possible to develop environmentally pure production with a closed cycle.

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